Retrievals of ethane from ground-based high-resolution FTIR solar observations with updated line parameters: determination of the optimum strategy for the Jungfraujoch station.

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1. Introduction

• Ethane (C_2H_6) is the most abundant Non-Methane HydroCarbon (NMHC) in the Earth's atmosphere, with a lifetime of approximately 2 months. C_2H_6 main sources are biomass burning, natural gas loss and biofuel consumption. Oxidation by the hydroxyl radical is by far the major C_2H_6 sink and the OH seasonality controls the strong modulation of the ethane abundance throughout the year. Ethane reduces Cl atom concentrations in the lower stratosphere and is a major source of peroxyacetyl nitrate (PAN) and carbon monoxide (by reaction with OH). Involved in the formation of tropospheric ozone and in the destruction of atmospheric methane through competition in OH consumption, C_2H_6 is an indirect greenhouse gas with a net-global warming potential of 5.5 (100-yr horizon).

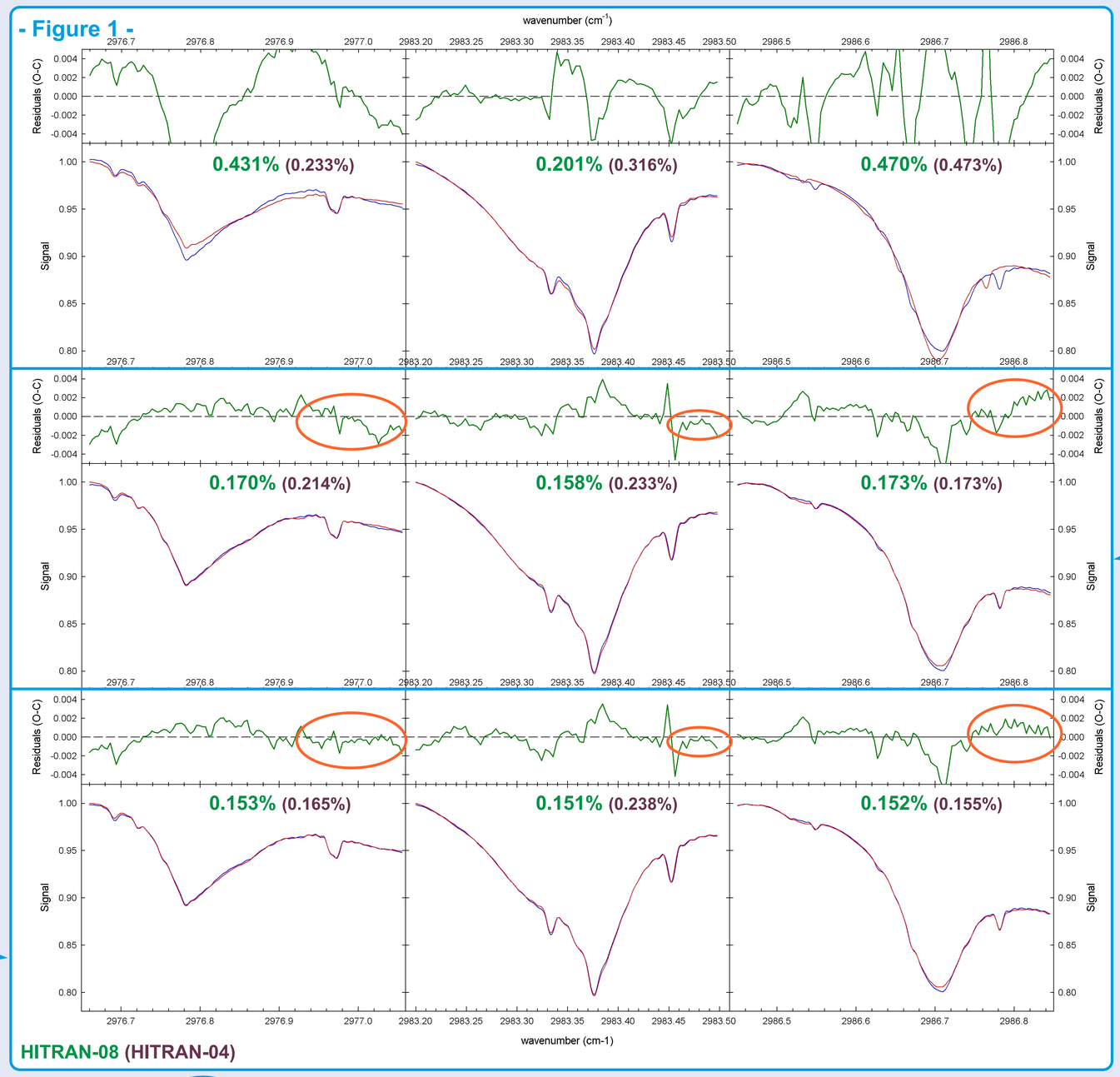
• All the spectra analyzed here have been recorded at the International Scientific Station of the Jungfraujoch (46.5°N, 8°E, 3580 m asl) with a Bruker IFS-120HR Fourier Transform Infrared (FTIR) spectrometer. This instrument is in regular operation since 1994, allowing to record wide-band high-resolution IR solar spectra either with a MCT or InSb detector. The FTIR instrument is affiliated to the Network for the Detection of Atmospheric Composition Change (NDACC, visit http://www.ndacc.org).

2. Retrieval Strategy

• All retrievals have been performed with the SFIT-2 algorithm (v 3.91) (Rinsland et al., 1998) in order to determine three ethane vertical partial columns (see Figure 2) from a series of about 13 000 spectra recorded between 1994 and 2011. The adopted settings are : (i) three spectral intervals ranging from 2976.66 to 2977.059 ($_pQ^3$), from 2983.2 to 2983.5 and from 2986.45 to 2986.85 cm^{-1} ; (ii) the C_2H_6 volume mixing ratio (vmr) *a priori* profile and uncertainties issued from the CHASER Model (Chemical AGCM for Study of atmospheric Environment and Radiative Forcing - Sudo et al., 2002), a priori profiles for the interfering gases (i.e. H_2O, CH_4, O_3 and CH_3Cl) based on the WACCM model climatology ; (iii) HITRAN 2008 line parameters including Harrison's pseudo lines, the two O_3 lines update provided by P. Chelin (Personal Communication, 2004) and the updated CH_3Cl lines (Bray et al., 2011) for target and interfering absorptions ; (iv) temperature and geopotential height data sets provided by the National Centers for Environmental Prediction (NCEP, Washington, USA).

• As the state of ethane parameters in HITRAN (e.g.: Rothman et al., 2009, http://www.hitran.com) was rather unsatisfactory in the 3µm region, new C_2H_6 spectroscopic parameters were awaited in order to reproduce ethane spectra in a more acurate and precise way. Here, three updated linelists have been tested, for C_2H_6 and two interfering species (CH_3Cl, O_3). The effect on our residuals is illustrated on Figure 1.

- Figure 1 - Mean observed (blue curve)/simulated (red curve) spectra and residuals (green curve) for 187 spectral fits (4.96 mK) of our three microwindows. Spectroscopic linelists used are HITRAN-08 (first row), HITRAN-08 combined with Harrison's C_2H_6 updated parameters as well as P. Chelin's O_3 update (second row -see text frame A) and HITRAN-08 combined with Harrison's, P. Chelin's and Bray's updated CH_3Cl lines (third row -see text frame B). Residual values are displayed for both HITRAN-08 (green values) and HITRAN-04 (purple values).



(A) - Both spectroscopic updates are used.

• The first one, see Harrison *et al.* (2010), is issued from a new set of high resolution IR spectra of ethane recorded with and without additional synthetic air at the Molecular Spectroscopy Facility of the Rutherford Appleton Laboratory using a high-resolution FTIR spectrometer. IR absorption cross sections for ethane have been measured in the 3 µm spectral region and were calibrated in intensity by using reference low-resolution spectra from the Pacific Northwest National Laboratory (PNNL, Washington, USA, http://www.pnl.gov/) IR database. They were combined with both HITRAN 2004 and 2008 line parameters and therefore used in our retrievals, after conversion into pseudolines by G. C. Toon.

• The second one consists in the update of two O_3 lines (encompassed in the $_pQ^3$ µ-window) corrected by P. Chelin (LPMA, Paris, France) in the framework of the UFTIR project.

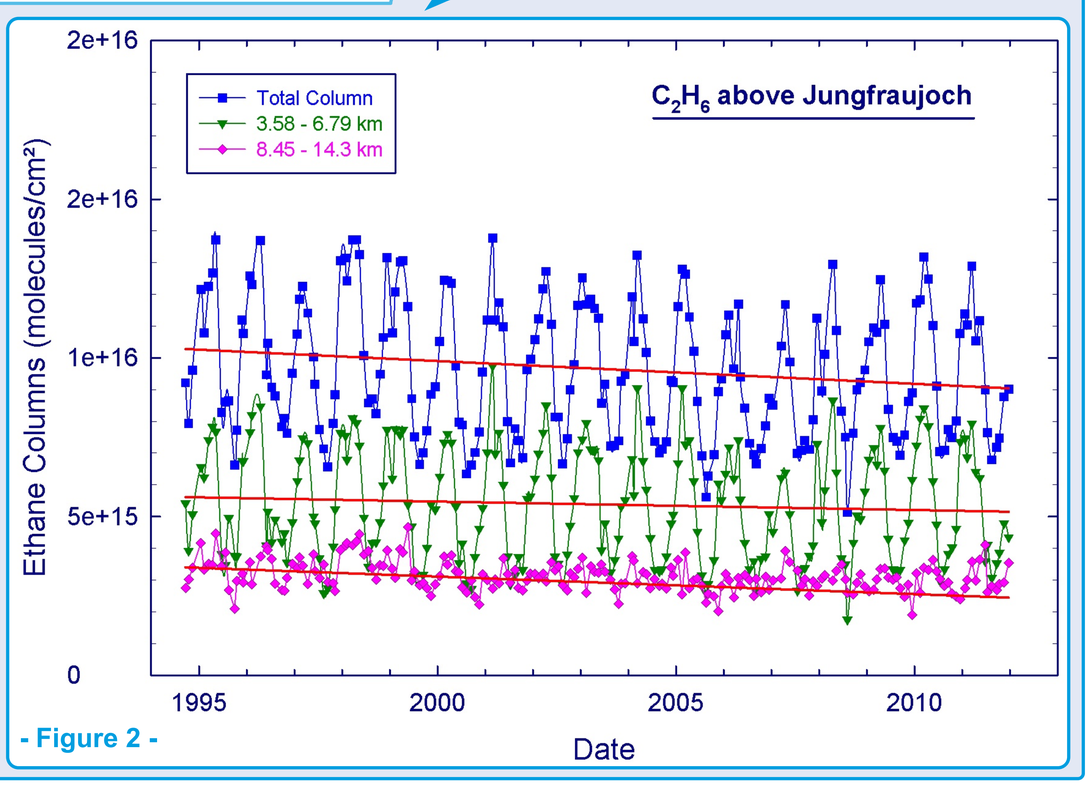
(B) - The linelist included in the spectroscopic parameters we used is an update of the CH_3Cl line positions and line intensities for the v_1, v_4 and $3v_6$ in the 3.4 µm region, see Bray *et al.* (2011 & 2012). Fourier transform spectra have been recorded at high resolution at the Laboratoire de Dynamique, Interactions et Réactivité in France. Measurements of line positions and line intensities have been performed for both isotopologues $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$ in the v_1, v_4, $3v_6$ bands. Line intensities were compared to the recent integrated intensities from PNNL.

3. Time Series

• The Figure 2 displays our retrieved C_2H_6 total and partial columns (low-tropospheric and UTLS) above Jungfraujoch. We computed an overall decrease in ethane concentrations since 1994 of -14, -9 and -39 % resp. for our three columns. Trends have been determined using the boostrap resampling tool developed by Gardiner *et al.* (2008).

• Our measurements allow to characterize the strong seasonal variations of C_2H_6 total and low-tropospheric columns with a maximum generally observed around mid-February. On average, the peak-to-peak amplitudes respectively amount to 50 and 76 % of the 1994 reference column.

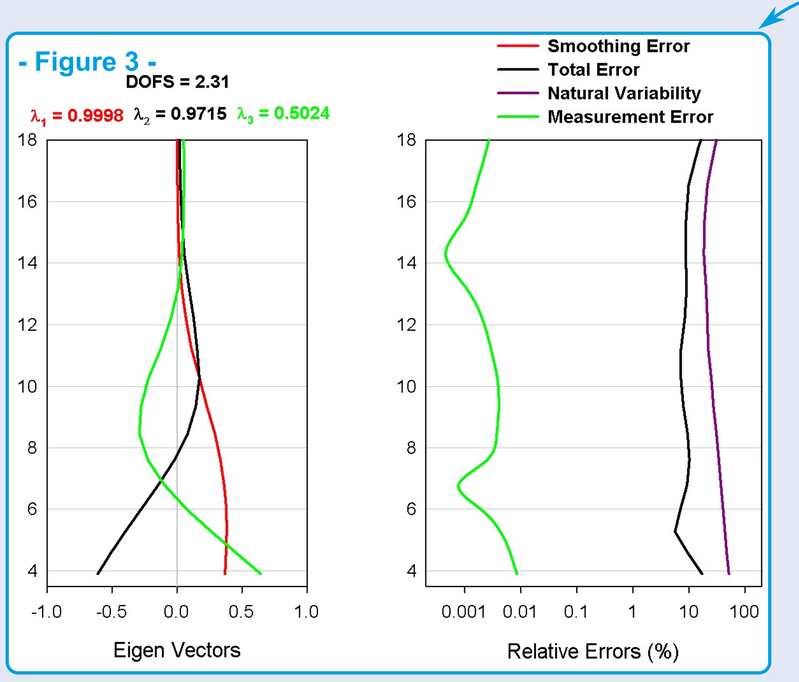
- Figure 2 - Time series of C_2H_6 total column (in blue), low-tropospheric (3.58-6.79 km, in green) and UTLS (8.45-14.3 km, in pink) partial columns above Jungfraujoch. Red lines are linear trends.



4. Information Content

• Figure 3 displays typical results computed for the vmrs. The first eigen vectors and corresponding eigenvalues (see left frame, in red) show that information on both selected C_2H_6 partial columns, namely 3.58-6.79 km (low-tropospheric) and 8.45-14.3 km (Upper Tropospheric-Lower Stratospheric, UTLS), is mainly coming from the retrieval (99 %).

- Figure 3 - Information content calculated for typical C_2H_6 retrievals at the Jungfraujoch station. The three first eigenvectors are reproduced in the left frame. Right frame gives the corresponding error budget, with identification of the main error components, together with the assumed variability (see color codes).



- Table 1 -

Columns		Total	Low-Tropo	UTLS
Solar Zenith Angle		0.04 %	0.16 %	0.14 %
Temperature		0.88 %	3.61 %	3.69 %
Line parameters uncertainties	H_2O	0.10 %	0.29 %	0.18 %
	O_3	0.04 %	0.11 %	0.09 %
	CH_4	0.13 %	0.52 %	0.32 %
	C_2H_6	0.69 %	0.88 %	0.79 %

5. Error Budget

- Table I - The establishment of a complete error budget is still ongoing, preliminary error analysis is displayed in this table.

• We have already quantified the impact on our retrieved C_2H_6 columns of the uncertainty on the solar zenith angle, on the NCEP temperature profiles and on the line intensities of the interfering species through sensitivity tests (values on Table 1). The uncertainties on the solar zenith angle are estimated at 0.2° while error quantities associated with temperature uncertainties are provided by the NCEP.

• Error on line intensities is provided by uncertainty indices reported on HITRAN-08, Rothman *et al.* (2009 and references therein). Therefore, according to these indices we have included line intensities in our retrievals modified by 2 % for the H_2O lines, by 2 or 5 % for the O_3 line and by 10 % for the CH_4 line. We observe a seasonal variation of the error on temperature with a maximum during Spring (10 %) and a minimum (< 0.6 %) during Autumn.

• An error of 4% on the intensity of C_2H_6 has been reported by Harrison *et al.* (2010) while the error issued from the conversion into pseudolines has been evaluated to 4% (Rinsland *et al.*, 2012). Therefore, a combined direct systematic bias of about 8% may affect our C_2H_6 column retrievals.

6. Conclusions and Perspectives

• Harrison's new ethane parameters coupled to HITRAN-08 compilation as well as Chelin's O_3 and Bray's CH_3Cl updates improve the retrieval of ethane in terms of spectral residuals and information content.
• We opted for the HITRAN-08 compilation for the interfering species (except CH_3Cl) as it showed better residuals than the HITRAN-04 parameters.
• Concerning the long-term trend of C_2H_6, we determined a significant decrease in its concentration over the 1994-2011 time period. We also characterized a seasonal change in total and tropospheric columns of ethane greater than the previously mentionned decrease.
• We expect to put more investigations into the study of the interannual variations as well as of the seasonal change of ethane in the lower-troposphere and in the UTLS region.

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